

## Preparation of flexible slabstock foam polyols

The present invention relates to a process for preparing  
5 polyether alcohols, to the polyether alcohols prepared by this  
process and to their use for producing polyurethanes.

Polyether alcohols are used in large quantities for producing  
polyurethanes. They are usually prepared by catalytic addition of  
10 lower alkylene oxides, in particular ethylene oxide and propylene  
oxide, onto H-functional initiator substances. Catalysts used are  
usually basic metal hydroxides or salts, with potassium hydroxide  
having the greatest practical importance.

15 The alkylene oxides are usually added on as a block or as a  
random mixture. In the blockwise molecular addition, only one  
alkylene oxide at a time is added on, while in the random  
molecular addition, a mixture of alkylene oxides is present in  
the reaction mixture.

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In the industry, ethylene oxide and propylene oxide are usually  
used as alkylene oxides, since they are readily available and  
inexpensive. The reactivity of ethylene oxide is higher than that  
of propylene oxide, so that the molecular addition of ethylene  
25 oxide proceeds at a higher reaction rate. To increase the  
space-time yield in the preparation of polyether alcohols it  
would be desirable for the proportion of ethylene oxide in the  
polyether alcohol to be as high as possible. Provision of  
polyether alcohols which are intended for use in flexible foams  
30 with terminal ethylene oxide blocks is known and customary. The  
associated increase in the number of primary hydroxyl groups in  
the polyether alcohols results in an increase in their reactivity  
in the reaction with polyisocyanates. However, the increase in  
the ethylene oxide content of the polyether alcohol also results  
35 in an increase in the hydrophilicity of the polyether alcohol,  
which can lead, inter alia, to undesirable gel formation in the  
polyether alcohols.

Furthermore, in the synthesis of polyether alcohols having long  
40 chains, as are used for producing flexible polyurethane foams,  
increasing chain growth is associated with secondary reactions  
which lead to defects in the chain structure. These by-products  
are referred to as unsaturated constituents and lead to a  
deterioration in the properties of the resulting polyurethanes.  
45 Many attempts have therefore been made in the past to prepare  
polyether alcohols having a low content of unsaturated  
constituents. In particular, the alkoxylation catalysts used have

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been altered in a targeted way in an attempt to achieve this. Thus, EP-A-268 922 proposes using cesium hydroxide. Although this enables the content of unsaturated constituents to be reduced, cesium hydroxide is expensive and disposing of it is  
5 problematical.

Furthermore, the use of multimetal cyanide complexes, usually zinc hexacyanometalates, also known as DMC catalysts, for preparing polyether alcohols having low contents of unsaturated  
10 constituents is also known. There is a large number of documents in which the preparation of such compounds is described. Thus, DD-A-203 735 and DD-A-203 734 describe the preparation of polyetherols using zinc hexacyanocobaltate.

15 The preparation of the zinc hexacyanometalates is also known. These catalysts are usually prepared by reacting solutions of metal salts such as zinc chloride with solutions of alkali metal or alkaline earth metal cyanometalates, e.g. potassium hexacyanocobaltate. A water-miscible, heteroatom-containing  
20 component is generally added to the resulting suspension immediately after the precipitation step. This component can also be present initially in one or both starting solutions. This water-miscible, heteroatom-containing component can be, for example, an ether, polyether, alcohol, ketone or a mixture  
25 thereof. Such processes are described, for example, in US 3,278,457, US 3,278,458, US 3,278,459, US 3,427,256, US 3,427,334, US 3,404,109.

Polyether alcohols used for producing flexible slabstock foams  
30 generally have a complete propylene oxide inner block which can make up as much as 40% by weight of the total polyol bound directly to the initiator substance and on this propylene oxide inner block have mixed blocks of propylene oxide and ethylene oxide which make up at least 60% by weight of the total polyol  
35 and contain at least 2% by weight of ethylene oxide. These polyols are generally prepared using basic catalysts. WO-A-97/27,236 describes the preparation of a flexible slabstock foam polyol in which at least one propylene oxide inner block is added on using multimetal cyanides as catalyst. However, this  
40 process does not permit a further increase in the ethylene oxide content of the polyether alcohol without the abovementioned disadvantages.

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It is an object of the present invention to develop polyether alcohols which have a high ethylene oxide content without there being a significant increase in the hydrophilicity of the product.

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We have found that this object is achieved by a polyether alcohol which can be prepared by ring-opening polymerization of ethylene oxide and alkylene oxides having at least 3 carbon atoms, which comprises an inner block of ethylene oxide or a mixture of  
10 ethylene oxide and alkylene oxides having at least 3 carbon atoms, and attached to this a block comprising at least one alkylene oxide having at least 3 carbon atoms or a mixture of ethylene oxide and alkylene oxides having at least 3 carbon atoms, preferably propylene oxide, where the mixed blocks  
15 preferably contain at least 2% by weight and not more than 20% by weight of ethylene oxide, based on the mixture.

The present invention accordingly provides polyether alcohols which can be prepared by ring-opening polymerization of ethylene  
20 oxide and propylene oxide onto H-functional initiator substances, wherein not more than 40% by weight, based on the weight of the polyether alcohol, of ethylene oxide or a mixture of ethylene oxide and alkylene oxides having at least 3 carbon atoms, where the mixture has an ethylene oxide content of at least 98% by  
25 weight, based on the mixture, is added onto the initiator substance and subsequently at least one alkylene oxide having at least 3 carbon atoms or a mixture of ethylene oxide and at least one alkylene oxide having at least 3 carbon atoms, where the mixture has a maximum ethylene oxide content of 20% by weight,  
30 based on the mixture, is added on.

If a mixture of ethylene oxide and at least one alkylene oxide having at least 3 carbon atoms is added on, the content of ethylene oxide should be at least 0.5% by weight, based on the  
35 mixture.

As alkylene oxides having at least 3 carbon atoms in the molecule, preference is given to using propylene oxide, butylene oxide and isobutylene oxide and also any mixtures of at least two  
40 of the alkylene oxides mentioned, particularly preferably propylene oxide.

In a preferred embodiment of the present invention, ethylene oxide can be added onto the polyether alcohol at the end of the  
45 chain, i.e. after the molecular addition of the alkylene oxides having at least 3 carbon atoms or of the mixture of ethylene oxide and alkylene oxides having at least 3 carbon atoms. The

amount of this ethylene oxide added onto the end of the chain is preferably not more than 15% by weight, based on the weight of the polyether alcohol. Such polyether alcohols are preferably used for producing cold-cure polyurethane foams. Polyether  
5 alcohols of the present invention without this ethylene oxide end block are preferably used for producing flexible polyurethane foams, in particular flexible slabstock foams.

It has surprisingly been found that the hydrophilicity of the  
10 polyether alcohols of the present invention is significantly lower than that of conventional polyether alcohols containing the same amount of ethylene oxide in the polyether chain but having a different distribution of alkylene oxides in the chain.

15 The present invention further provides a process for preparing the above-described polyether alcohols. The polyether alcohols of the present invention are prepared by ring-opening polymerization of the alkylene oxides ethylene oxide and the alkylene oxides having at least 3 carbon atoms onto H-functional initiator  
20 substances in the presence of catalysts.

In a preferred embodiment of the process of the present invention, the molecular addition of the total amount of alkylene oxide is carried out in the presence of basic catalysts. Basic  
25 catalysts which can be used are, for example, amines, basic salts, metal oxides and metal hydroxides. Preference is given to using alkali metal and/or alkaline earth metal hydroxides. In industry, potassium hydroxide is usually used.

30 In a further preferred embodiment of the process of the present invention, multimetal cyanides, frequently also referred to as DMC catalysts, are used as catalyst for the molecular addition of the alkylene oxides. The advantages of using these catalysts are firstly the higher reaction rate in the molecular addition of the  
35 alkylene oxides and secondly the fact that the polyether alcohols prepared in this way have a lower content of unsaturated constituents. However, this embodiment has the disadvantage that there can be a delayed start of the reaction at the beginning when using DMC catalysts.

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In further preferred embodiments of the process of the present invention, the various sections of the polyether chain are added on using different catalysts. Thus, it is advantageous to add on an ethylene oxide block at the beginning of the chain using basic  
45 catalysts and to add on the subsequent block consisting entirely or predominantly of alkylene oxides having at least 3 carbon atoms using DMC catalysts. The ethylene oxide block which may, if

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desired, be present at the end of the chain can likewise be added on by means of DMC catalysts, but preferably by means of basic catalysts. This procedure has the advantage that the delay which frequently occurs at the start of the reaction when using  
 5 multimetal cyanide catalysts is avoided. This is balanced by increased costs due to the additional purification step.

When using different catalysts, it may be necessary to purify the polyether alcohol to remove catalyst prior to changing the  
 10 catalysts. Particularly when changing from basic catalysts to DMC catalysts, a thorough purification is usually carried out because traces of the basic catalyst, in particular the alkali metal hydroxides customarily used, can poison the DMC catalyst.

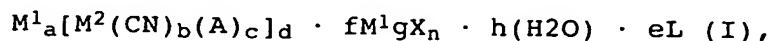
15 The invention further provides polyurethanes which can be produced by reacting polyisocyanates with compounds having at least two hydrogen atoms which are reactive toward isocyanate groups, wherein the polyether alcohols of the present invention are used as compounds having at least two hydrogen atoms which  
 20 are reactive toward isocyanate groups. The polyether alcohols of the present invention are preferably used for producing flexible polyurethane foams, with the polyether alcohols without a terminal ethylene oxide block being used, in particular, for producing slabstock foams and hot-cure molded foams and the  
 25 polyether alcohols having a terminal ethylene oxide block being used, in particular, for producing cold-cure molded foams.

As initiator substances for preparing the polyetherols of the present invention, use is made of the customary polyfunctional  
 30 alcohols having from 2 to 8 hydroxyl groups in the molecule. In particular, 2- and/or 3-functional alcohols, for example ethylene glycol, propylene glycol, glycerol or trimethylolpropane, are used for preparing polyether alcohols as are customarily used for producing flexible polyurethane foams.

35 The polyether alcohols of the present invention preferably have a molecular weight in the range from 1000 to 100,000.

Alkylenes used are, as indicated above, ethylene oxide and  
 40 alkylenes having at least 3 carbon atoms, in the abovementioned ratios.

The multimetal cyanides used as catalysts in the process of the present invention usually have the formula (I)  
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where

M<sup>1</sup> is a metal ion selected from the group consisting of Zn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>3+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Sn<sup>2+</sup>, Pb<sup>2+</sup>, Mo<sup>4+</sup>, Mo<sup>6+</sup>, Al<sup>3+</sup>, V<sup>4+</sup>, V<sup>5+</sup>, Sr<sup>2+</sup>, W<sup>4+</sup>, W<sup>6+</sup>, Cr<sup>2+</sup>, Cr<sup>3+</sup>, Cd<sup>2+</sup>,

M<sup>2</sup> is a metal ion selected from the group consisting of Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Co<sup>3+</sup>, Mn<sup>2+</sup>, Mn<sup>3+</sup>, V<sup>4+</sup>, V<sup>5+</sup>, Cr<sup>2+</sup>, Cr<sup>3+</sup>, Rh<sup>3+</sup>, Ru<sup>2+</sup>, Ir<sup>3+</sup>

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and M<sup>1</sup> and M<sup>2</sup> are identical or different,

A is an anion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, thiocyanate, isocyanate, cyanate, carboxylate, oxalate and nitrate,

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X is an anion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, thiocyanate, isocyanate, cyanate, carboxylate, oxalate and nitrate,

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L is a water-miscible ligand selected from the group consisting of alcohols, aldehydes, ketones, ethers, polyethers, esters, ureas, amides, nitriles and sulfides,

25 and

a, b, c, d, g and n

are selected so that the compound is electrically neutral, and

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e is the coordination number of the ligand,

f is a fraction or integer greater than or equal to 0 and

35 h is a fraction or integer greater than or equal to 0.

These compounds are prepared by generally known methods by combining the aqueous solution of a water-soluble metal salt with the aqueous solution of a hexacyanometalate compound, in particular a salt or an acid, and adding a water-soluble ligand thereto during or after the mixing of the solutions.

Owing to their high activity, the multimetal cyanide compounds are very well suited to the synthesis of the polyether alcohols of the present invention. The catalyst concentrations used are less than 1% by weight, preferably less than 0.5% by weight, particularly preferably less than 1000 ppm, in particular less

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than 500 ppm, very particularly preferably less than 100 ppm, based on the total mass of the polyether polyol prepared. The preparation of the polyether alcohols by means of the multimetal cyanide compounds can be carried out either continuously or  
5 batchwise. The synthesis can be carried out in suspension, in a fixed bed, in a moving bed or in a fluidized bed.

As far as the reaction conditions pressure and temperature are concerned, there is no difference in principle between catalysis  
10 by means of basic compounds and by means of multimetal cyanide compounds. The molecular addition of the alkylene oxides is carried out at from 50°C to 200°C, preferably from 90°C to 150°C, and at pressures in the range from 0.001 bar to 100 bar, preferably from 0.001 bar to 20 bar for the molecular addition of  
15 alkylene oxides having at least 3 carbon atoms in the molecule and preferably from 1 to 40 bar for the molecular addition of ethylene oxide. Before introducing the alkylene oxides, the reaction vessel is usually made inert by flushing with an inert gas, for example nitrogen.

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The molecular addition of the alkylene oxides is usually followed by an after-reaction phase in order to effect complete reaction of the alkylene oxides.

25 After the reaction, the polyether alcohol formed is worked up in a customary fashion by firstly removing unreacted alkylene oxide and other volatile constituents from the crude polyether alcohol by stripping or distillation and, if necessary, removing suspended material and/or mechanical contamination by means of  
30 filtration.

If the last process step was base-catalyzed, the catalyst has to be removed as usual from the polyether alcohol. For this purpose, the basic catalyst is usually neutralized with an acid and the  
35 salts formed are removed from the polyether alcohol by means of filtration.

If the last process step has been catalyzed using multimetal cyanide compounds, the catalyst can in principle remain in the  
40 polyether alcohol, but it can also be removed if necessary, for example by means of filtration.

The polyether alcohols of the present invention are very well suited to the production of polyurethanes, in particular flexible  
45 polyurethane foams. They are very readily compatible with the other constituents of the polyurethane formulations and have, despite their comparatively high content of ethylene oxide units

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in the polyether chain, a low hydrophilicity. Owing to the higher reaction rate of the polymerization of ethylene oxide compared to propylene oxide, the space-time yield in the preparation of the polyether alcohols of the present invention is higher than that  
5 in the case of conventional polyether alcohols for the same application areas. A further increase in the space-time yield can be achieved when at least part of the alkylene oxides is added on using multimetal cyanide compounds as catalyst.

10 The invention is illustrated by the following examples:

Examples 1 and 2

Addition of ethylene oxide onto an initiator substance

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Example 1

1115 g of glycerol and 32.5 g of a 47% strength aqueous potassium hydroxide solution were placed in a 10 l reactor. The water was  
20 removed at 95-100°C under a reduced pressure of less than 1 mm of mercury over a period of 1.5 hours. At 110°C and a nitrogen prepressure of 3.5 bar abs., 3980 g of ethylene oxide were metered in over a period of 6 hours. After reaction was complete, a water pump vacuum was applied, 250 g of Ambosol® magnesium  
25 silicate and 50 g of water were subsequently added to remove the catalyst and the polyether alcohol was subsequently filtered and dewatered by means of distillation.

The polyether alcohol formed had the following properties:

30 hydroxyl number: 394 mg KOH/g, viscosity at 25°C: 240 mPa\*s, potassium content: 5 ppm.

Example 2

35 The procedure of Example 1 was repeated, but 612 g of glycerol, 31.7 g of a 47% strength aqueous potassium hydroxide solution and 4356 g of ethylene oxide were reacted.

The polyether alcohol formed had the following properties:

40 hydroxyl number: 219 mg KOH/g, viscosity at 25 °C: 222 mPa\*s, potassium content: 3 ppm.

## Examples 3 and 4

## Preparation of the polyether alcohols

- 5 The syntheses were carried out in a 10 l stirred reactor. This was charged with the reaction products from Examples 1 and 2 at 50°C. The contents of the reactor were made inert by evacuating three times and each time filling with nitrogen. Degassing was carried out by evacuation at 105°C and a pressure of less than
- 10 1 mbar abs. for 1.5 hours. A double metal cyanide catalyst from the reaction of zinc acetate with hexacyanocobaltic acid and tert-butanol were then added. The reactor was again evacuated three times and each time filled with nitrogen. This was followed by evacuation to a pressure of less than 1 mbar abs. for about
- 15 half an hour with the temperature being increased to 125°C. At this temperature, a mixture of propylene oxide and ethylene oxide was added. After a further 30 minutes at 125°C, the polyether alcohol formed was freed of volatile constituents under reduced pressure. To remove the catalyst, the polyether alcohol was
- 20 filtered through a double layer of a Seitz deep filter (K 900).

The amounts of starting materials used and the properties of the polyether alcohols prepared are shown in Table 1.

## 25 Result:

All polyether alcohols have an inner block of glycerol and ethylene oxide. In Example 3, this is adjoined by a mixed block of ethylene oxide and propylene oxide, in Example 4 by a block of

30 propylene oxide.

Polyether alcohols which have only a small proportion of unsaturated constituents were obtained. Products having a very low hydroxyl number can also be obtained by the process of the

35 present invention. The polyether alcohols have narrow molecular weight distributions in all cases.

Table 1  
Amounts of starting materials used and analyses of the polyether alcohols prepared

Exam- ple	Polyether from Example	Amount of polyether [g]	Catalyst [g]	Propyle- ne oxide [g]	Ethylene oxide [g]	Hydroxyl number [mgKOH/g]	Viscosity at 25 °C [mPa*s]	M <sub>n</sub> [g]	M <sub>w</sub> [g]	Unsaturated constituents [meq/g]
3	1	609.7	2.141	4288	107	47.1	722	2877	3093	0.0066
4	2	1097.3	2.142	3909	-	46.3	725	2849	3004	0.0058

Examples 5 (comparative example) and 6

#### Production of foams

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In Comparative Example 5 and Example 6, the polyol and isocyanate components shown in Table 2 were reacted to produce flexible polyurethane foams. The constituents of the polyol component were intensively mixed. The isocyanate component was then added while  
10 stirring and the reaction mixture was poured into an open mold in which it foamed to form the polyurethane foam.

The product properties of the polyurethane foam of the present invention are likewise summarized in Table 2. The testing  
15 standards used are shown in Table 3.

Table 2:

Production and properties of flexible slabstock foams

20			Example 5 (C)	Example 6
	Polyol component	Hydroxyl number [mgKOH/g]	Amount [g]	Amount [g]
25	Polyol A	48	1000	
	Polyol from Example 4	48		1000
	Water	6233	38	38
30	BF 2370		10	10
	Amine catalyst N 201	560	1,9	1.9
	Amine catalyst N 206	426	0.6	0.6
	Tin catalyst K 29	0	2.3	2.5
35	Total		1053	1053.0
	Isocyanate component	NCO [%]	Amount [g]	Amount [g]
	TDI 80/20	48.3	488.0	488.0
	Index		110	110
40	Test data	Unit		
	Cream time	[s]	15	10
	Fiber time	[s]	90	80
45	Rise time	[s]	90	85
	Rise height	[mm]	275	265

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	Rise height after 5 min	[mm]	270	260
	Air permeability	[mmWs]	10	10
	Foam density	[kg/m <sup>3</sup> ]	25.3	26.4
5	Compressive strength at 40% compression	[kPa]	4.7	4.1
	Tensile strength	[kPa]	79,1	88
	Elongation	[%]	121	146
10	Compressive set at 50% compression	[%]	2.4	2.4

15 Polyol A: Glycerol-initiated polyether alcohol having an inner block of 30 parts by weight of propylene oxide and an adjoining mixed block of 57 parts by weight of propylene oxide and 10 parts by weight of ethylene oxide.

Table 3: Testing standards

20	<b>Test method</b>	<b>Standard</b>
	Foam density	DIN 53420
	Tensile test (tensile strength, elongation)	DIN 53571
25	Compressive set	DIN 53572
	Rebound resilience	DIN 53573
	Indentation hardness	DIN 53576
30	Compressive strength	DIN 53577

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